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ORIGINAL ARTICLE

Spectroscopic and semiempirical investigation of the structural features of hetarylazo-5-isoxazolones tautomerism

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Abstract 3-Methyl-4-hetarylazo-5-isoxazolones (I–IV) have been synthesized and investigated on the basis of Fourier transform infrared (FT-IR), UV–visible (UV–Vis), proton nuclear magnetic resonance (^{1}H NMR) spectroscopic techniques and elemental analysis. The measured FT-IR and ^{1}H NMR spectra together with the theoretical calculations (semiempirical) showed that the investigated compounds exist in the hydrazone-keto form in the solid state and chloroform. However, the measured UV–Vis electronic absorption spectra in solutions clarified that the hetarylazo-5-isoxazolone dyes possess equilibrium between hydrazone-keto and common anion forms depending upon the nature of the medium. Furthermore, these dyes display a broad absorption band in the visible region (between 370 and 435 nm) which could be assigned to π–π^* transition with a considerable intramolecular charge transfer (CT) character.

1. Introduction

Azo dyes represent an extraordinary family of compounds not only for their biological activity [1–4], extensive applications in the dye industry [5], analytical reagents and metallochromic indicators [6], but also for their interesting structural and physicochemical properties [4–7]. Currently, heteroarylazoisoxazole compounds have received the attention of many research groups [8–12], because of their widespread potential applications in fields such as catalysis [9], cancer treatment, using as antibacterial and antiviral agents, agricultural fungicides as well as other biological uses [10–12]. Recently, the demand for such a group of compounds has been increased due to the use of these compounds as optical and conducting organic materials [13–15]. In the light of these findings we focused on the synthesis, tautomerism and spectroscopic properties of some novel heteroarylazoisoxazolone dyes

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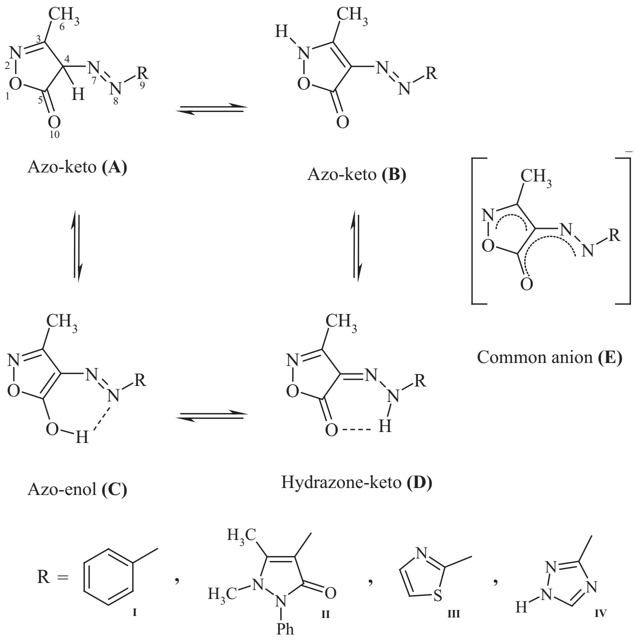
using experimental spectral data combined with theoretical calculations (semiempirical).

2. Experimental

2.1. Synthesis of the azoisoxazolone compounds (I–IV)

Dyes (I–IV) under investigation (Scheme 1) were prepared according to the procedure described in the literature [16–18]. To an ice-cooled stirred solution of the appropriate amine (0.01 mol) (aniline, 4-aminoantipyrine (4-aminophenazone), 2-aminothiazole and 3-amino-1,2,4-triazole) dissolved in diluted HCl (~30 ml; 50%), a cold solution of $NaNO_2$ (0.01 mol) was added gradually with stirring for 20 min. To a cold solution of 3-methyl-5-isoxazolone (0.01 mol) in ethanol in the presence of sodium acetate, a solution of the diazotized amine was added dropwise with vigorous stirring at 0–5 °C for 35 min. After addition, stirring was continued for 1 h, and the obtained precipitate was filtered off and washed with cold water and ethanol. The solid products were recrystallized from hot ethanol to give the corresponding azo dyes (II–IV). However, compound (I) was recrystallized from warm benzene. Azo dyes (I–IV) were dried in vacuo over silica gel (yield = 40–50%). The chemical structures of the prepared dyes were checked by elemental analysis, IR and ^1H NMR spectra (Tables 1 and 2).



Scheme 1 Expected tautomeric forms and common anion of the azo dyes (I–IV).

2.2. Apparatus and techniques

The UV–Vis spectra were recorded in the range of 200–800 nm on a Shimadzu 2401 PC spectrophotometer using 1-cm matched quartz cells. The IR spectra were obtained as KBr disks on a Nicolet FT-IR 560 (4000–200 cm^{-1}) spectrophotometer. The ^1H NMR ($CDCl_3$) spectra were recorded on a Varian Mercury VX-300 MHz instrument. All chemicals used were of pure grade (BDH, Aldrich or Sigma products). Spectrograde solvents were used for spectral measurements. The pH measurements were carried out on JENWAY MODEL 3051 digital pH meter accurate to ±0.02 pH unit. All the measurements were carried out at room temperature (≈20 °C). The full geometry optimization of the tautomers of the dyes (Fig. 1) in the gas phase was carried out at the level of semiempirical methods PM6 [19], AM1 and PM3 [6,20–22]. Solvent effects on tautomers were also investigated using PM6 (COSMO) model [19] as implemented in MOPAC 2009 [23]. All calculations were done on a Pentium IV PC computer.

Table 1 Microchemical analysis data and melting points of the synthesized azo dyes (I–IV).

Comp.	Empirical formula	Mol. wt.	m.p. (°C)	Color	%Found (calculated)			
					C	H	N	S
I	$C_{10}H_9N_3O_2$	203	188–190	Yellow crystals	58.97 (59.11)	4.44 (4.43)	20.71 (20.68)	–
II	$C_{15}H_{15}N_5O_3$	313	210–212	Red crystals	57.28 (57.44)	4.71 (4.79)	22.20 (22.34)	–
III	$C_7H_6N_4O_2S$	210	198–200	Dark brown powder	39.98 (40.00)	2.85 (2.85)	26.56 (26.66)	15.07 (15.23)
IV	$C_6H_6N_6O_2$	194	230–232	Yellow powder	37.03 (37.11)	3.07 (3.09)	43.30 (43.29)	–

Table 2 IR and ^1H NMR spectral data of the investigated azo dyes (I–IV).

Comp.	IR ν (cm^{-1})					^1H NMR (δ, ppm)
	ν(NH)	ν(C=O)	ν(C=N)	ν(C=C)	ν(C–O)	In $CDCl_3$
I	3225	1720	1575	1490	1145	12.67 (s, 1H, NH), 7.24–7.48 (m, 5H-Ar), 2.34 (s, 3H, $-CH_{3(isoxazole)}$)
II	3100	1700, 1659	1570	1485	–	7.26–7.52 (m, 5H-Ar), 3.17 (s, 3H, N-CH_3), 2.53 (s, 3H, $-CH_{3(pyrazole)}$), 2.27 (s, 3H, $-CH_{3(isoxazole)}$)
III	3110	1750	1545	1486	–	7.05 (d, 1H, $-CH_{(thiazole)}$), 7.52 (d, 1H, $-CH_{(thiazole)}$), 2.32 (s, 3H, $-CH_{3(isoxazole)}$)
IV	3200	1730	1575	1490	1140	8.35 (s, 1H, $-CH_{(triazole)}$), 2.18 (s, 3H, $-CH_{3(isoxazole)}$)